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THERMALLY STIMULATED PROCESSES

Thermally stimulated processes (TSP) are comprised of catalyzing the processes of charge generation and its storage in the condensed phase at a relatively higher temperature and freezing the created charges, mainly in the bulk of the dielectric material, at a lower temperature. The agency for creation of charges may be derived by using a number of different techniques; Luminescence, x-rays, high electric fields corona discharge, etc. The external agency is removed after the charges are frozen in and the material is heated in a controlled manner during which drift and redistribution of charges occur within the volume. During heating one or more of the parameters are measured to understand the processes of charge generation. The measured parameter, in most cases the current, is a function of time or temperature and the resulting curve is variously called as the glow curve, thermogram or the heating curve. In the study of thermoluminescence the charge carriers are generated in the insulator or semiconductor at room temperature using the photoelectric effect.

The experimental aspects of TSP are relatively simple though the number of parameters available for controlling is quite large. The temperature at which the generation processes are catalyzed, usually called the poling temperature, the poling field, the time duration of poling, the freezing temperature (also called the annealing temperature), and the rate of heating are examples of variables that can be controlled. Failure to take into account the influences of these parameters in the measured thermograms has led to conflicting interpretations and in extreme cases, even the validity of the concept of TSP itself has been questioned.

In this chapter we provide an introduction to the techniques that have been adopted in obtaining the thermograms and the methods applied for their analysis. Results obtained in specific materials have been used to exemplify the approaches adopted and indicate

the limitations of the TSP techniques^{1, 2, 3}. To limit the scope of the chapter we limit ourselves to the presentation of the Thermally Stimulated Depolarization (TSD) Current.

In what follows we adopt the following terminology:

The electric field, which is applied to the material at the higher temperature, is called the poling field. The temperature at which the generation of charges is accelerated is called the poling temperature and, in polymers, mostly the approximate glass transition temperature is chosen as the poling temperature.

The temperature at which the electric field is removed after poling is complete is called the initial temperature because heating is initiated at this temperature.

The temperature at which the material is kept short circuited to remove stray charges, after attaining the initial temperature and the poling field is removed, is called the annealing temperature. The annealing temperature may or may not be the initial temperature.

The current released during heating is a function of the number of traps (n_t). If the current is linearly dependent on n_t then first order kinetics is said to apply. If the current is dependent on n_t^2 (Van Turnhout, 1975) then second order kinetics is said to apply.

10.1 TRAPS IN INSULATORS

The concept of traps has already been introduced in chapter 7 in connection with the discussion of conduction currents. To facilitate understanding we shall begin with the description of thermoluminescence (Chen and Kirsch, 1981). Let us consider a material in which the electrons are at ground state G and some of them acquire energy, for which we need not elaborate the reasons, and occupy the level E (Fig. 10.1). The electrons in the excited state, after recombinations, emit photons within a short time interval of 10^{-8} s and return to the ground state. This phenomenon is known as fluorescence and emission of light ceases after the exciting radiation has been switched off.

The electrons may also lose some energy and fall to an energy level M where recombination does not occur and the life of this excited state is longer. The energy level corresponding to M may be due to metastables or traps. Energy equivalent to ϵ needs to be imparted to shift the electrons from M to E, following which the electrons undergo recombination. In luminescence this phenomenon is recognized as delayed emission of light after the exciting radiation has been turned off. In the study of TSDC and TSP the energy level corresponding to M is, in a rather unsophisticated sense, equivalent to traps

of single energy. The electrons stay in the trap for a considerable time which results in delayed response.

The probability of acquiring energy, ϵ_a , thermally to jump from a trap may be expressed as

$$\frac{n}{n_0} = s \exp\left(-\frac{\epsilon_a}{kT}\right) \quad (10.1)$$

where n is the number of electrons released at temperature T , n_0 the initial number of traps from which electrons are released ($n/n_0 \leq 1$), s is a constant, k the Boltzmann constant and T the absolute temperature. Eq. (10.1) shows that the probability increases with increasing temperature. The constant s is a function of frequency of attempt to escape from the trap, having the dimension of s^{-1} . A trap is visualized as a potential well from which the electron attempts to escape. It acquires energy thermally and collides with the walls of the potential well. s is therefore a product of the number of attempts multiplied by the reflection coefficient. In crystals it is about an order of magnitude less than the vibrational frequency of the atoms, $\sim 10^{12} s^{-1}$.

The so called first order kinetics is based on the simplistic assumption that the rate of release of electrons from the traps is proportional to the number of trapped electrons. This results in the equation

$$\frac{dn}{dt} = -\alpha n(t) \quad (10.2)$$

where the constant, α represents the decrease in the number of trapped electrons and has the dimension of s^{-1} . The solution of eq. (10.2) is

$$n(t) = n_0 \exp(-\alpha t) \quad (10.3)$$

where n_0 is the number of electrons at $t = 0$.

In terms of current, which is the quantity usually measured, equation (10.3) may be rewritten as

$$I = -C \left(\frac{dn}{dt} \right) = C \frac{n}{\tau} \exp\left(-\frac{\epsilon_a}{kT}\right) \quad (10.4)$$

where τ is called the relaxation time, which is the reciprocal of the jump frequency and C a proportionality constant. Let us assume a constant heating rate β . We then have

$$T = T_0 + \beta t \quad (10.5)$$

where T_0 and t are the initial temperature and time respectively.

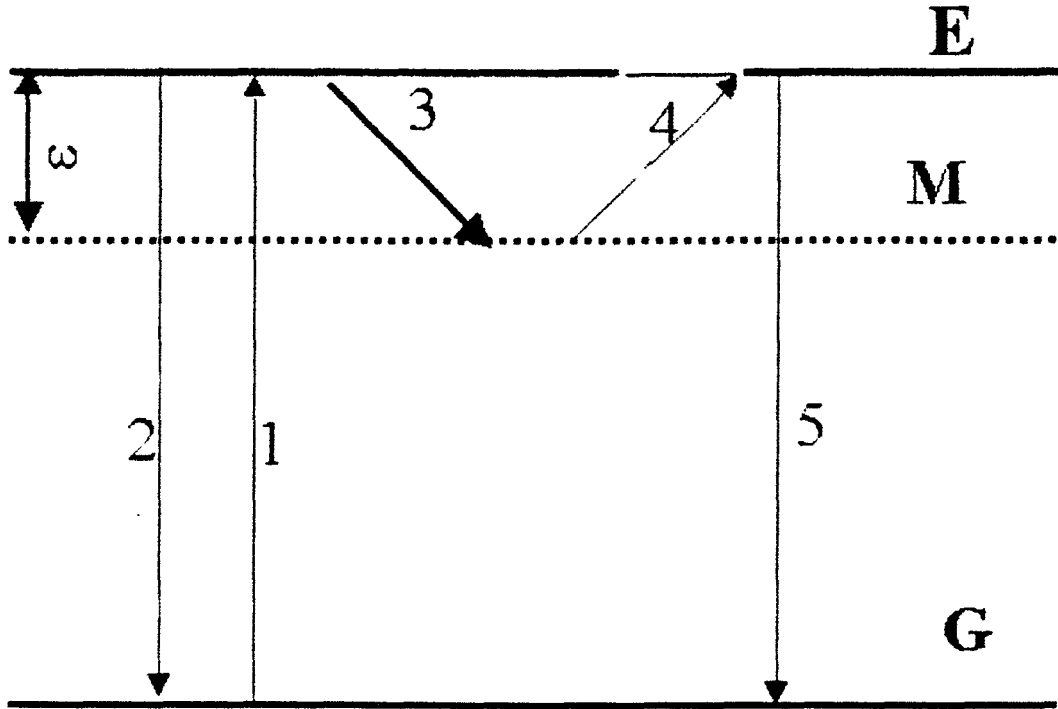


Fig. 10.1 Energy states of electrons in a solid. G is the ground state, E the excited level and M the metastable level. Excitation shifts the electrons to E via process 1. Instantaneous return to ground state-process 2 results in fluorescence. Partial loss of energy transfers the electron to M via process 3. Acquiring energy ε the electron reverts to level E (process 4). Recombination with a hole results in the emission of a photon (Process 5) and phosphorescence. Adopted from Chen and Kirsch (1981), (with permission of Pergamon Press)

The solution of equation (10.4) is given as

$$I(T) = \frac{n_0}{\tau} \exp\left(-\frac{\varepsilon_a}{kT}\right) \exp\left[\left(-\frac{1}{\beta\tau}\right) \int_{T_0}^T \exp\left(-\frac{\varepsilon_a}{kT'}\right) dT'\right] \quad (10.6)$$

This equation is known as the first order kinetics. The second order kinetics is based on the concept that the rate of decay of the trapped electrons is dependent on the population

of the excited electrons and vacant impurity levels or positive holes in a filled band. This leads to the equation

$$I = -\frac{dn}{dt} = -\frac{n^2}{\tau'} \exp\left(-\frac{\varepsilon_a}{kT}\right) \quad (10.7)$$

where τ' is a constant having the dimension of $m^3 s^{-1}$. The solution of this equation is

$$I(T) = \frac{n_o^2}{\tau'} \exp\left(-\frac{\varepsilon_a}{kT}\right) \left[1 + \left(\frac{n_o}{\tau' \beta} \right) \int \exp\left(-\frac{\varepsilon_a}{kT'}\right) dT' \right]^{-2} \quad (10.8)$$

without losing generality, equations (10.6) and (10.8) are expressed as

$$I(t) = -\frac{dn}{dt} = \left(\frac{n}{n_o} \right)^b \frac{n_o}{\tau} \exp\left(-\frac{\varepsilon_a}{kT}\right) \quad (10.9)$$

where the exponent b is the order of kinetics.

Returning to Fig. (10.1) the metastable level M may be equated to traps in which the electrons stay a long time relative to that at E . The trapping level, having a single energy level ε , and a single retrapping center (Fig. 10.1) shows a single peak in the measured current as a function of the temperature. The trap energy level is determined, according to equation (10.1) for n_T , by the slope of the plot of $\ln(I)$ versus $1/T$.

A polymer having a single trap level and recombination center is a simplified picture, used to render the mathematical analysis easier. In reality, the situation that one obtains is shown in Fig. 10.2 where n_c denotes the number of electrons in the conduction band. The trap levels, $T_1, T_2, \dots$ are situated closer to the conduction band and the holes, $H_1, H_2, \dots$ are retrapping centers. Introduction of even this moderate level of sophistication requires that the following situations should be considered (Chen and Kirsch, 1981).

1. The trap levels have discrete energy differences in which case each level could be identified with a distinct peak in the thermogram. On the other hand the trap levels may form a local continuum in which case the current at any temperature is a contribution of a number of trap levels. The peak in the thermogram is likely to be broad.
2. The traps are relatively closer to the conduction band so that thermally activated electron transfer can occur. The holes are situated not quite so close to the valence

band so that the holes do not contribute to the current in the range of temperatures used in the experiments. The reverse situation, though not so common, may obtain; the holes are closer to the valence band and traps are deep. The electron traps now become recombination centers completing the “mirror image”.

3. The essential feature of a thermogram is the current peak, which is identified with the phenomenon of trapping and subsequent release due to thermal activation. The sign of the carrier, whether it is a hole or electron, is relatively of minor significance. In this context the trapping levels may be thermally active in certain ranges of temperature while, in other ranges, they may be recombination centers.
4. An electron which is liberated from a trap may drift under the field before being trapped in another center that has the same energy level. The energy level of the new trap may be shallower, that is closer to the conduction band. This mode of drift has led to the term “hopping”.

The development of adequate theories to account for these complicated situations is, by no means, straight forward. However, certain basic concepts are common and they may be summarized as below:

- 1) The intensity of current is a function of the number of traps according to equation 10.4. The implied condition that the number density of traps and holes is equal is not necessarily true. To render the approach general let us denote the number of traps by n_t and the number of holes by n_h . The number of holes will be less if a free electron recombines with a hole. Equation (10.7) now becomes

$$I = -\frac{dn_h}{dt} = f_{rc} n_h n_c \quad (10.10)$$

where n_c is the number density of free carriers in the conduction band and f_{rc} is the recombination probability with the dimension of $m^3 s^{-1}$. The recombination probability is the product of the thermal velocity of free electrons in the conduction band, v , and the recombination cross section of the hole, σ_{rc} .

- 2) The electrons from the traps move to the conduction band due to thermal activation. The change in the density of trapped carriers, n_t , is dependent on the number density of trapped charges and the Boltzmann factor. Retrapping also reduces the number that moves into the conduction level. The retrapping probability is dependent on the number density of unoccupied traps. Unoccupied trap density is given by $(N-n_t)$ where N is the concentration of traps under consideration. The rate of decrease of electrons from the traps is given by

$$-\frac{dn_t}{dt} = sn_t \exp\left(-\frac{\varepsilon}{kT}\right) - n_c (N - n_t) f_{rt} \quad (10.11)$$

where f_{rt} is the retrapping probability ($\text{m}^3 \text{s}^{-1}$). Similar to the recombination probability, we can express f_{rt} as the product of the retrapping cross section, σ_{rt} , and the thermal velocity of the electrons in the conduction band.

3) The net charge in the medium is zero. Accordingly

$$n_c + n_t - n_h = 0 \quad (10.12)$$

This equation transforms into

$$\frac{dn_h}{dt} = \frac{dn_t}{dt} + \frac{dn_c}{dt} \quad (10.13)$$

Substituting equation (10.11) in (10.13) gives

$$\frac{dn_c}{dt} = sn \exp\left(-\frac{\varepsilon}{kT}\right) - n_c (n_h f_{rc} + (N - n_t) f_{rt}) \quad (10.14)$$

Equations (10.10), (10.13) and (10.14) are considered to be generally applicable to thermally stimulated processes, with modifications introduced to take into account the specific conditions. For example the charge neutrality condition in a solid with number of trap levels, $T_1, T_2, \dots$ etc., and a number of hole levels $H_1, H_2 \dots$ etc., (Fig. 10.2) is given by

$$\sum n_{tr} + n_c + \sum n_{hj} = 0 \quad (10.15)$$

Numerical solutions for the kinetic equations governing thermally stimulated are given by Kelly, et al. (1972) and Haridoss (1978)^{4, 5}. Invariably some approximations need to be made to find the solutions and Kelly, et al. (1971) have determined the conditions under which the approximations are valid. The model employed by them is shown in Fig. 10.3. Let N number of traps be situated at depth E below the conduction band, which has a density of states, N_c . On thermal stimulation the electrons are released from the traps to the conduction band with a probability lying between zero and one, according to the Boltzmann factor $e^{-E/kT}$.

The electrons move in the conduction band under the influence of an electric field, during which event they can either drop into recombination centers with a capture

coefficient γ or be retrapped with a coefficient of β . The relative magnitude of the two coefficients depend on the nature of the material; retrapping is dominant in dielectrics whereas recombination with light output dominates in thermoluminescent materials.

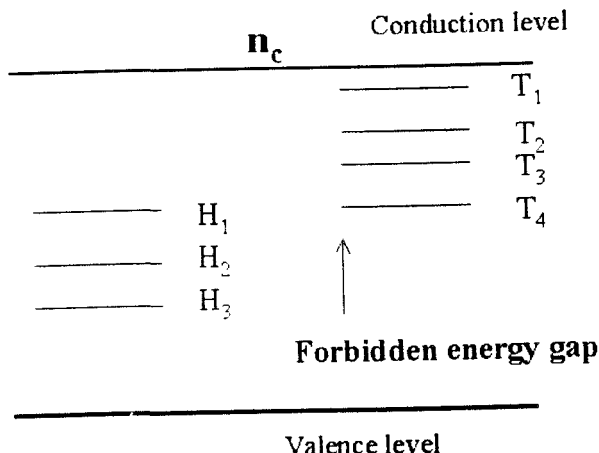


Fig. 10.2 Electron trap levels (T) and hole levels (H) in the forbidden gap of an insulator. N_c is the number density of electrons in the conduction band. The number density of electrons in T_1 is denoted by the symbol n_{t1} and hole density in H_1 is n_{h1} . Charge conservation is given by equation (10.15). Adopted from (Chen and Kirsch, 1981, with permission of Pergamon Press, Oxford).

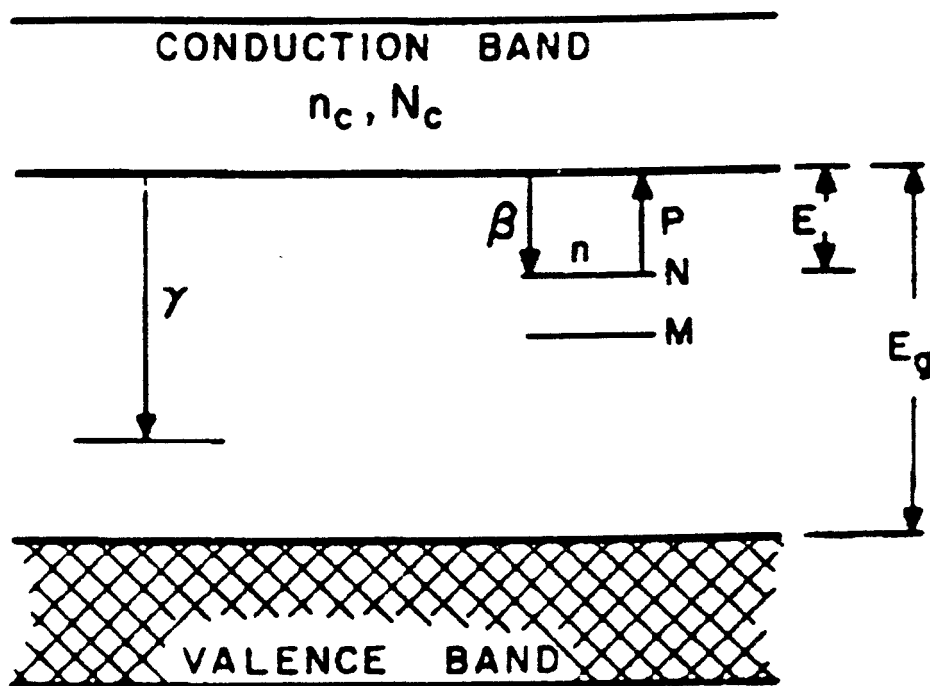


Fig. 10.3 Energy level diagram for the numerical analysis of Kelly et. al. (1972), (with permission of Am. Inst. of Phy.)

In the absence of deep traps, the occupation numbers in the traps and the conduction band are n and n_c respectively. Note that the energy diagram shown in fig. 10.3 is relatively more detailed than those shown in Figs. 10.1 and 10.2.

10.2 CURRENT DUE TO THERMALLY STIMULATED DEPOLARIZATION (TSDC)

We shall focus our attention on the current released to the external circuit during thermally stimulated depolarization processes. To provide continuity we briefly summarize the polarization mechanisms that are likely to occur in solids:

- 1) Electronic polarization in the time range of $10^{-15} \leq t \leq 10^{-17}$ s
- 2) Atomic polarization, $10^{-12} \leq t \leq 10^{-14}$ s
- 3) Orientational polarization, $10^{-3} \leq t \leq 10^{-12}$ s
- 4) Interfacial polarization, $t > 0.1$ s
- 5) Drift of electrons or holes in the inter-electrode region and their trapping
- 6) Injections of charges into the solid by the electrodes and their trapping in the vicinity of the electrodes. This mechanism is referred to as electrode polarization.

Considering the orientational polarization first, generally two experimental techniques are employed, namely, single temperature poling (Fig. 10.4) and windowing⁶ (Fig. 10.5). The windowing technique, also called fractional polarization, is meant to improve the method of separating the polarizations that occur in a narrow window of temperature. The width of the window chosen is usually 10°C. Even in the absence of windowing technique, several techniques have been adopted to separate the peaks as we shall discuss later on. Typical TSD currents obtained with global thermal poling and window poling are shown in figs. 10-6⁷ and 10-7⁸, respectively.

Bucci et. al.⁹ derived the equation for current due to orientational depolarization by assuming that the polar solid has a single relaxation time (one type of dipole). Mutual Interaction between dipoles is neglected and the solid is considered to be perfect with no other type of polarization contributing to the current. It is recalled that the orientational polarization is given by

$$P_{\mu} = \frac{1}{3} \frac{N \mu^2 E_p}{k T_p} \quad (2.51)$$

where E_p is the applied electric field during poling and T_p the poling temperature.

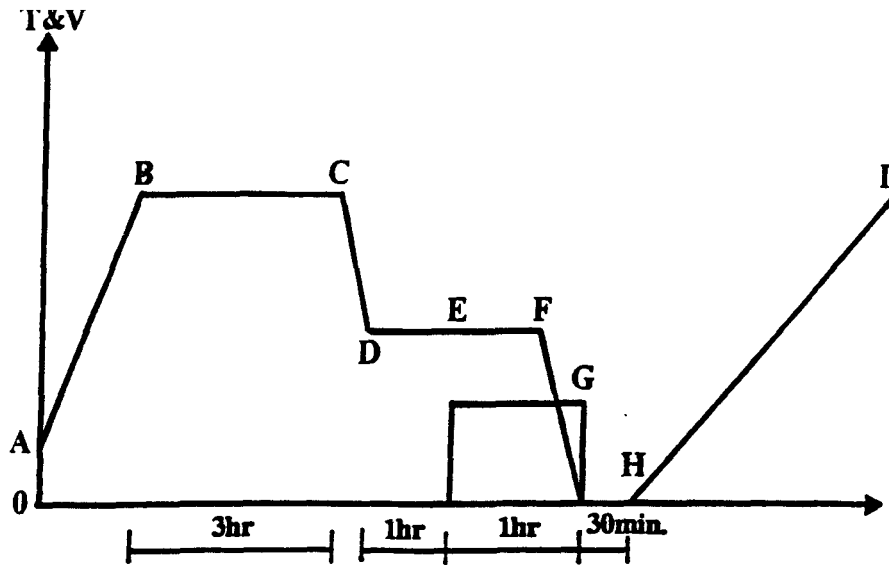


Fig. 10.4 Thermal protocol for TSD current measurement. AB-initial heating to remove moisture and other absorbed molecules, BC-holding step, time duration and temperature for AB-BC depends on the material, electrodes etc. CD-cooling to poling temperature, usually near the glass transition temperature, DE-stabilizing period before poling, electrodes short circuited during AE, EF-poling, FG-cooling to annealing temperature, GH-annealing period with electrodes short circuited, HI-TSD measurements with heating rate of β .

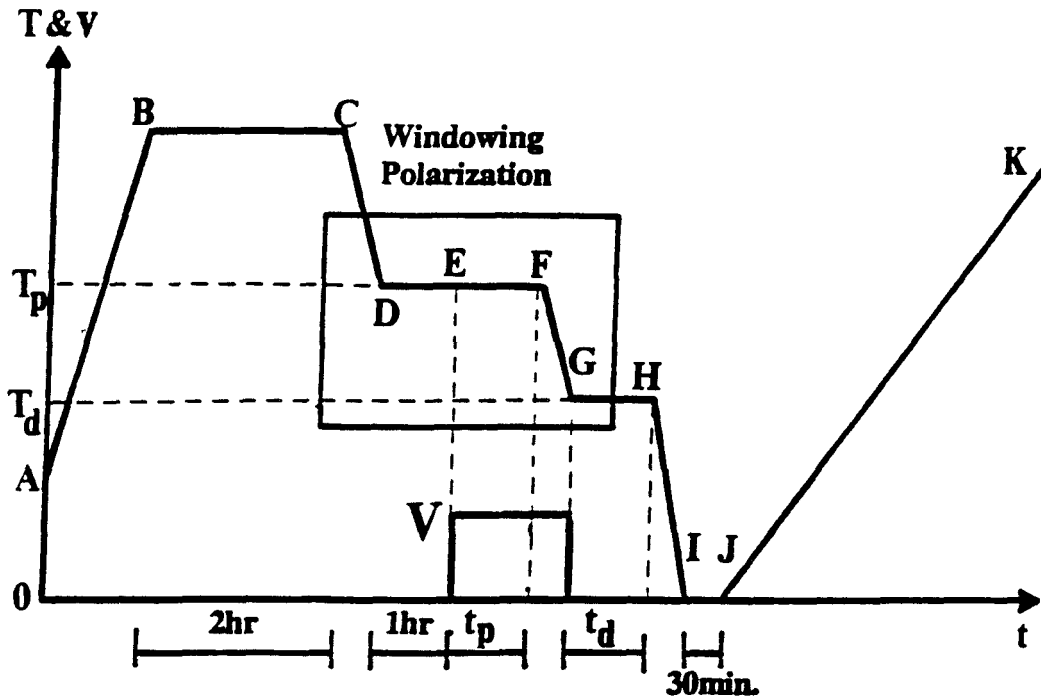


Fig. 10.5 Protocol for windowing TSD. Note the additional detail in the region EFGH. T_p and T_d are poling and window temperatures respectively. t_p and t_d are the corresponding times, normally $t_p = t_d$.

The relaxation time which is characteristic of the frequency of jumps of the dipole is related to the temperature according to

$$\tau = \tau_o \exp \frac{\varepsilon}{kT} \quad (10.16)$$

where $1/\tau$ (s^{-1}) is the frequency of a single jump and τ_o is independent of the temperature. Increasing the temperature decreases the relaxation time according to equation (2.51), as discussed in chapters 3 and 5.

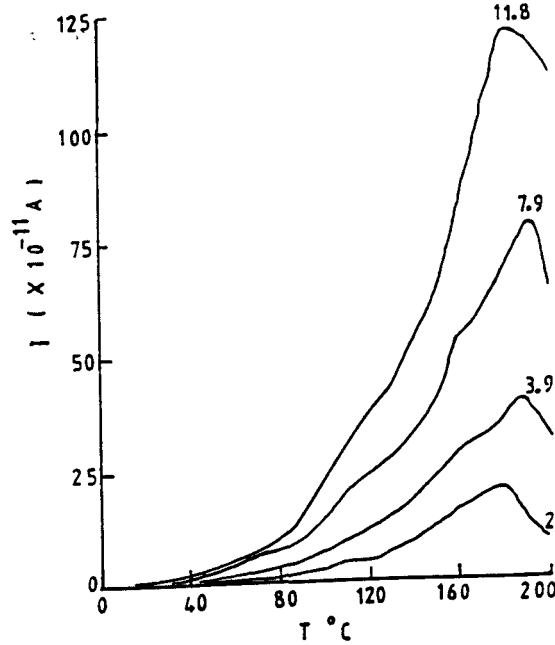


Fig. 10.6 TSD currents in 127 μm thick paper with $\beta = 2\text{K/min}$. The poling temperature is 200°C and the poling field is as shown on each curve, in MV/m .

The decay of polarization is assumed proportional to the polarization, yielding the first order differential equation

$$-\frac{dP(t)}{dt} = \frac{P(t)}{\tau(T)} = \frac{P(t)}{\tau_o} \exp\left(-\frac{\varepsilon}{kT}\right) \quad (3.10)$$

The solution of equation (3.10) may be written in the form¹⁰

$$P(T) = P_o \exp\left(-\frac{1}{\beta} \int_{T_o}^T \frac{dT'}{\tau(T')}\right) \quad (10.17)$$

The current density is given by

$$J = -\frac{dP}{dt} \quad (10.18)$$

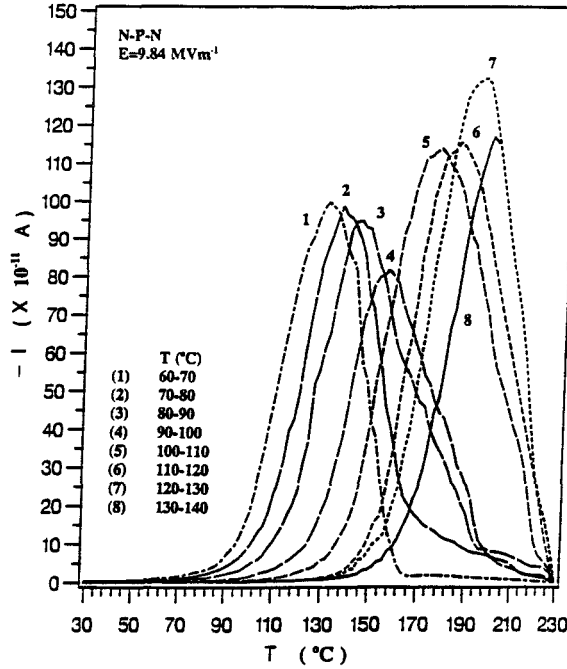


Fig. 10.7 TSD currents in a composite dielectric Nomex-Polyester-Nomex with window poling technique (Sussi and Raju. With permission of SAMPE Journal)

Assuming that the heating rate is linear according to

$$T = T_0 + \beta t \quad (10.19)$$

Using equation (10.16) this gives the expression for the current

$$J = \frac{P_\infty}{\tau} \exp \left(-\frac{1}{\beta \tau} \int_{T_0}^T \exp \left(-\frac{\varepsilon}{kT'} \right) dT' \right) \quad (10.20)$$

where T_0 is the initial temperature (K), β the rate of heating (Ks^{-1}), t the time (s). Substituting equation (2.51) in (10.20) Bucci et. al (1966) derive the expression for the current density as:

$$J = \frac{N \mu^2 E_p}{3kT\tau_o} \exp\left(-\frac{\varepsilon}{kT}\right) \exp\left[-\left(\frac{1}{\beta\tau_o}\right) \int_{T_o}^T \exp\left(-\frac{\varepsilon}{kT'}\right) dT'\right] \quad (10.21)$$

Equation (10.21) is first order kinetics and has been employed extensively for the analysis of thermograms of solids. By differentiation the temperature T_m at which the current peak occurs is derived as

$$T_m = \left[\varepsilon \tau_o \exp\left(\frac{\varepsilon}{kT_m}\right) \right]^{1/2} \quad (10.22)$$

T_m is independent of the poling parameters E_p and T_p but dependent on β . The number density of the dipoles is obtained by the relation

$$N = \frac{3kT_p}{\mu^2 E_p} \int_{T_o}^{\infty} J(T') dT' \quad (10.23)$$

where the integral is the area under the J-T curve.

According to equation (10.21) the current density is proportional to the poling field at the same temperature and by measuring the current at various poling fields dipole orientation may be distinguished from other mechanisms.

The concentration of charge carriers n_t for the case of mono-molecular recombination (τ is constant) and weak retrapping is given by¹¹

$$n_t = \frac{2.7 J_m k T_m^2}{e L \beta \varepsilon_a} \quad (10.24)$$

where J_m is the maximum current density.

10.3 TSD CURRENTS FOR DISTRIBUTION OF ACTIVATION ENERGY

Bucci's equation (10.21) for TSD currents assumes that the polar materials possess a single relaxation time or a single activation energy. As already explained, very few materials satisfy this condition. Before considering the distributed activation energies, it

is simpler to consider the analysis of TSD current spectra using the theory developed by Frohlich^{12, 13}.

$$J(T) = \frac{P_o}{\tau_o} \exp \left[-\frac{\epsilon_a}{kT} - \frac{1}{\beta \tau_o} \int_{T_o}^T \exp \left(-\frac{\epsilon_a}{kT'} \right) dT' \right] \quad (10.25)$$

in which P_o is a constant related to the initial polarization. Using a single value of ϵ_a in equation (10.25) generates a spectrum which is asymmetric as a function of the temperature while the experimental data are symmetric (Sauer and Avakian, 1992). This is remedied by assigning a slight breadth to the distribution of energies. An alternative is to express the TSD current in the form

$$J(T) = \sum_{i=1}^n a_i J(T, \epsilon_{ai}) \quad (10.26)$$

The mean value of ϵ_{ai} is found to give a good fit to the data as that obtained by Bucci method.

Fig. 10.8 shows the TSD current in poly(ethyl methacrylate) (PEMA) in the vicinity of T_g using a poling temperature of 30°C (Sauer and Avakian, 1992). Application of the Bucci equation gives an activation energy of 1.4 eV. Application of equation (10.25) with $\epsilon_a = 1.2$ eV gives a poor fit. Application of equation (10.26) with $n = 3$ and $\epsilon_{a1} = 1.35$ eV, $\epsilon_{a2} = 1.37$ eV, $\epsilon_{a3} = 1.41$ eV, $a_1 = 47\%$, $a_2 = 41\%$, $a_3 = 12\%$ gives a fit which is comparable to a Bucci fit. A gaussian distribution shows considerable deviation at low temperatures indicating a slower relaxing entity. Non-symmetrical dipoles and dipoles of different kinds (bonds) as in polymers are reasons for a solid to have a distribution of relaxation times. Interacting dipoles result in a distribution of activation energies. In both cases of distribution of activation energies and distribution of relaxation times, the thermogram is much broader than that observed for single relaxation time and the TSD current is

$$J = \frac{N \mu^2 E_p}{3kT \tau_o} \int_0^\infty F(\epsilon) \exp \left[-\frac{\epsilon}{kT} - \frac{1}{\beta \tau_o} \int_{T_o}^T \exp \left(-\frac{\epsilon}{kT'} \right) dT' \right] d\epsilon \quad (10.27)$$

where $F(\epsilon)$ is the distribution function of activation energies. A similar equation for continuous distribution of pre-exponentials may be derived from equation (10.21).

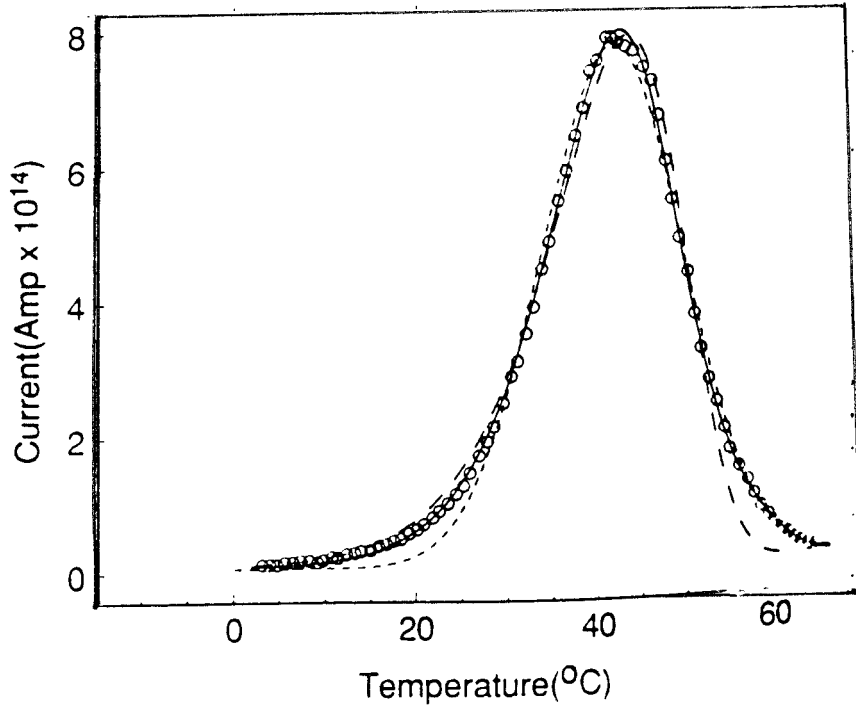


Fig. 10.8 TSD current in poly(ethyl methacrylate) poled near T_g . Fit to Frohlich's equation (10.25) is shown. Open circles: Experimental data; broken line: Frohlich's equation, single energy; full line: Frohlich's equation, distributed energy, G-Gaussian distribution.

10.4 TSD CURRENTS FOR UNIVERSAL RELAXATION MECHANISM

The dipolar orientation of permanent dipoles according to Debye process results in a TSD current according to equation (10.21). However we have seen in chapters 3 and 5 that the assumption of non-interacting dipoles has been questioned by Jonscher¹⁴ who has suggested a universal relaxation phenomenon according to fractional power laws:

(a) In the frequency range $\omega > \omega_p$:

$$\chi''(\omega) \propto \omega^m$$

(b) In the frequency range $\omega < \omega_p$:

$$\chi' = \chi_s - \tan(m\pi/2)\chi''(\omega)$$

$$\chi''(\omega) = \cot\left(\frac{n\pi}{2}\right) \chi'(\omega) \propto \omega^{n-1}$$

where the exponents m and n fall in the range (0,1). The TSD current in materials behaving in accordance with these relaxations is given by:

$$J(t) = aP_{\mu}\omega_p \left[\int_0^t \omega_p dt \right]^{-n} \quad \text{where } t < (1/\omega_p) \quad (10.28)$$

In the case of distribution of relaxation times and single activation energy the initial slopes are equal whereas a distribution of activation energies results in different slopes. Peak cleaning technique is employed to separate the various activation energies as will be demonstrated below, while discussing experimental results.

10.5 TSD CURRENTS WITH IONIC SPACE CHARGE

The origin of TSD currents is not exclusively dipoles because the accumulated ionic space charge during poling is also released. The decay of space charge is generally more complex than the disorientation of the dipoles, and Bucci, et al. bring out the following differences between TSD current characteristics due to dipoles and release of ionic space charge;

1. In the case of ionic space charge the temperature of the maximum current is not well defined. As T_p is increased T_m increases.
2. The area of the peak is not proportional to the electric field as in the case of dipolar relaxation, particularly at low electric fields.
3. The shape of the peak does not allow the determination of activation energy (Chen and Kirsch, 1981).

The derivation of the TSD current due to ionic space charge has been given by Kunze and Müller¹⁵. Let us suppose that the dark conductivity varies with temperature according to

$$\sigma = \sigma_0 \exp\left(-\frac{\varepsilon}{kT}\right) \quad (10.29)$$

and the heating rate is reciprocal according to

$$\frac{1}{T} = \frac{1}{T_0} - \beta t \quad (10.30)$$

$$-\frac{d(T^{-1})}{dt} = \frac{1}{T^2} \frac{dT}{dt} = a = \text{constant} \quad (10.31)$$

where T_0 and β are the initial temperature and heating rate ($\text{K}^{-1}\text{s}^{-1}$) respectively. The TSD current density is given by

$$J(t) = \frac{\sigma_0}{\epsilon\epsilon_0} Q_0 \exp\left(-\frac{\epsilon}{kT}\right) \exp\left[-\frac{\sigma_0}{\epsilon\epsilon_0\beta} \int_{T_0}^T \exp\left(-\frac{\epsilon}{kT'}\right) dT'\right] \quad (10.32)$$

where Q_0 is the charge density on the electrodes at temperature T_0 .

10.6 TSD CURRENTS WITH ELECTRONIC CONDUCTION

Materials which possess conductivity due to electrons or holes present additional difficulties in analyzing the TSD currents. The theory has been worked out by Müller¹⁶ who considered a dielectric (ϵ_1) under investigation sandwiched between insulating foils of dielectric constant ϵ_2 , and thickness d_2 . This arrangement prevents the superposition of current due to electron injection from the TSD current. The theory is relevant to these experimental conditions.

$$J(T) = \frac{f\sigma_0 P_0}{\epsilon_0\epsilon_2} \exp\left[-\frac{\epsilon}{kT} - \frac{f\sigma_0 k}{a\epsilon\epsilon_0\epsilon_2} \exp\left(-\frac{\epsilon}{kT}\right)\right] \quad (10.33)$$

The current peak is observed at

$$\frac{f\sigma_0 k}{a\epsilon\epsilon_0\epsilon_2} \exp\left(-\frac{\epsilon}{kT_m}\right) = 1 \quad (10.34)$$

where T_m is the temperature at the current maximum. The current peak is asymmetrical. The activation energy is determined by the equation

$$\ln \varepsilon = \ln \left(\frac{J_m}{aP_\mu} \right) + 1 \quad (10.35)$$

where J_m is the maximum current density and P_μ is determined from the area of the J-t curve.

10.7 TSD CURRENTS WITH CORONA CHARGING

The mechanism of charge storage in a dielectric may be studied by the measurements of TSD currents, and the theory for the current has been given by Creswell and Perlman¹⁷. Sussi and Raju¹⁸ have applied the theory to corona charged aramid paper. Let us assume a uniform charge density of free and trapped charge carriers, the charge in an element of thickness at a depth x and unit area is

$$dQ = \rho dx \quad (10.36)$$

in which ρ is the surface charge density. The contribution to the current in the external circuit due to release of this element of charge is [Creswell, 1970]

$$dJ = \frac{WdQ}{s} = \frac{J(x)dx}{s} \quad (10.37)$$

where s is the thickness of the material and J the current due to the element of charge, W the velocity with which the charge layer moves and $J(x)$ the local current due to the motion of charge carriers.

According to Ohm's law, the current density is

$$J(x) = \rho\mu E(x) \quad (10.38)$$

where μ is the mobility and $E(x)$ the electric field at a depth x . The electric field is not uniform due to the presence of space charges within the material and the field can be calculated using the Poisson's equation

$$\frac{dE}{dx} = \frac{\rho_1}{\varepsilon_0 \varepsilon_s} \quad (10.39)$$

where ρ_1 is the total charge density (free plus trapped) and ϵ_s is the dielectric constant of the material. If we denote the number of free and trapped charge carriers by n_f and n_t respectively, the current is given by

$$J = \frac{\mu e^2 \delta^2}{2\epsilon_s s} n_t (n_t + n_f) \quad (10.40)$$

in which δ is the depth of charge penetration, $\delta \ll x$ and e the electronic charge.

In general it is reasonable to assume that $n_f \ll n_t$ and equation (10.40) may be approximated to

$$J = \frac{\mu e^2 \delta^2}{2\epsilon_s s} n_t n_t \quad (10.41)$$

The released charge may be trapped again and for the case of slow retrapping Creswell and Perlman¹⁹ have shown that

$$J = \frac{\mu e^2 \delta}{2\epsilon_o \epsilon_s} \frac{n_{t0}}{\tau_o} \exp \left[\left(-\frac{\epsilon_a}{kT} - \frac{2}{\beta \tau_o} \right) \times \int_{T_o}^T \exp \left(-\frac{\epsilon_a}{kT} \right) dT \right] \quad (10.42)$$

where n_{t0} is the initial density of charges in traps, $1/\tau_o = \nu$ the attempt to escape frequency, ϵ_a the trap depth below the conduction band.

The relaxation time is related to temperature according to

$$\tau = \tau_o \exp \left(\frac{\epsilon_a}{kT} \right) \quad (3.59)$$

Equation (10.42) may be rewritten in the form

$$J = A \exp \left[-p + \beta \int \exp(-p) p^{-2} dp \right] \quad (10.43)$$

$$A = \left(\frac{\mu e^2 \delta^2 n_{t0}}{2\epsilon_o \epsilon_s} \right) \frac{\tau}{\tau_o} \quad (10.44)$$

$$B = \frac{2\varepsilon_a}{k\beta\tau_0} \quad (10.45)$$

$$p = \frac{\varepsilon_a}{kT} \quad (10.46)$$

For maximum current we differentiate equation (10.43) and equate it to zero to yield

$$B = p_{\max}^2 \exp(p_{\max}) \quad (10.47)$$

in which $p_{\max}$ is related to $T_{\max}$ according to equation (10.46).

Figure 10.9 (Creswell and Perlman 1970) shows the TSD currents in negatively charged Mylar with silver-paste electrodes, with several rates of heating. The spectra are complicated with a downward shift of the peak as the heating rate is lowered. By a partial heating technique the number of peaks and their magnitude were determined and Arrhenius plots were drawn as shown in Fig.10.10. The slope increases with increasing temperature and the activation energy varies in the range of 0.55 eV at 50°C to 2.2 eV at 110°C in four discrete steps. The low energy traps of 0.55 eV and 0.85 eV are electronic and the trap of depth 1.4 eV is ionic. The 2.2 eV trap is either ionic, interfacial or release of electron to conduction band by complex processes. In interpreting these results it is generally true that trap depths less than 1 eV are electronic and if greater than 1 eV they are ionic. Assuming that the traps are monomolecular trap densities of the order of $10^{22}/\text{m}^3$ are obtained.

Fig 10.11 shows the TSD currents in corona charged aramid paper (Sussi and Raju, 1994) which shows the complexity of the spectrum and considerable caution is required in interpreting the results.

10.8 COMPENSATION TEMPERATURE

The Arrhenius equation for the relaxation time, which is the inverse of jump frequency between two activated states, is expressed as

$$\tau = \tau_0 \exp \frac{\varepsilon}{kT} \quad (3.59)$$

where τ_0 is the pre-exponential factor. A plot of $\log \tau$ against $1/T$ yields a straight line according to equation (3.59) with a slope of the apparent activation energy, ϵ . For secondary or low temperature relaxation the activation energy is low in the range of 0.5 –1.0 eV and the values of τ_0 are generally on the order of 10^{-12} s. These ranges of values are found from thermally activated molecular motions. However, high values of ϵ and very low values of τ_0 are not associated with the picture of molecular jump between two sites separated by a energy barrier. These values of both high ϵ and low τ_0 are explained on the basis of cooperative movement corresponding to long range conformational changes, characteristic of the α -relaxation²⁰.

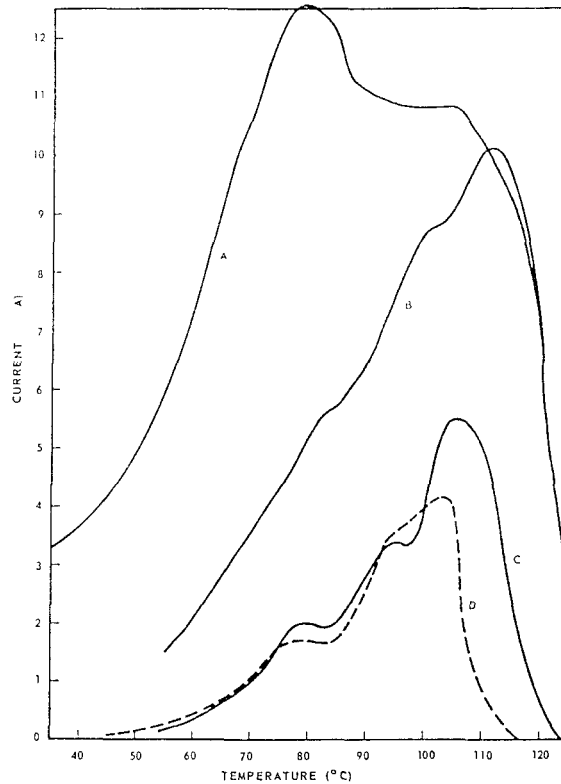


Fig. 10.9 Thermal current spectra for negatively corona-charged Mylar (2m). (a)- 1°/min, after 1.5 hr; (b)-1°/min after 24 hr; (c)- 0.4°/min, after 15 days; (d) at 0.2°/min after 25 days (Creswell and Perlman, 1970, with permission of American Institute of Physics.)

In many materials the plot of $\log \tau$ against $1/T$ tends to show lower activation energy, particularly at high temperatures. In this region the relaxation time is often represented by the Vogel-Tammann-Fulcher (VTF) law given by

$$\tau = \tau_0 \exp \frac{A}{(T - T_0)} \quad (10.48)$$

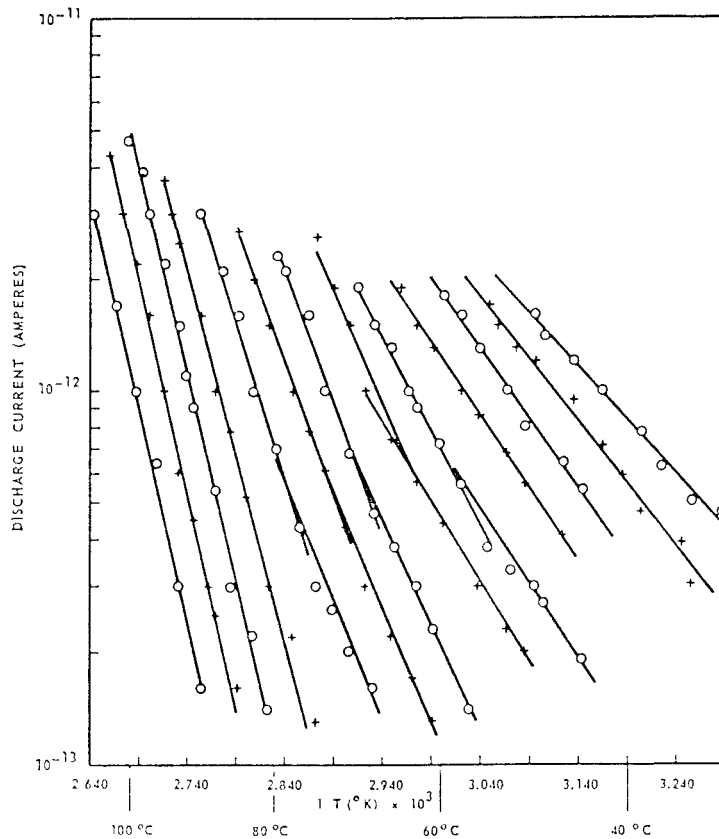


Fig. 10.10 Arrhenius plots of TSD currents in Mylar obtained by partial heating (Creswell and Perlman, 1970, with permission of American Inst. of Physics).

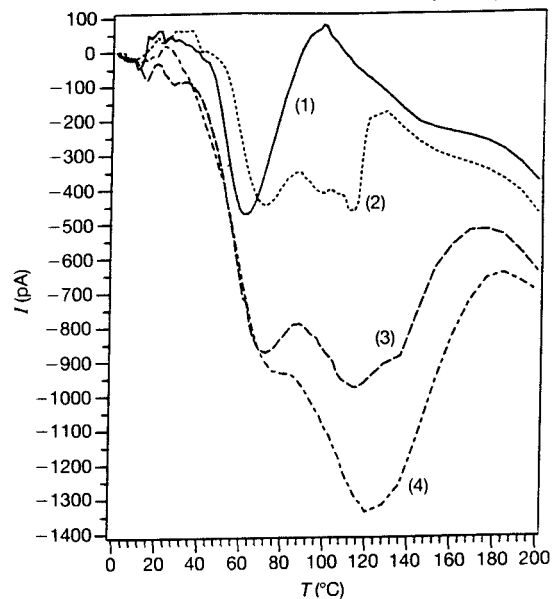


Fig. 10.11 TSD current in corona charged at 16.38 kV in 76mm aramid paper. Influence of electrode material is shown. Charging time and electrode material are: (1) 10 min., Al. (2) 10 min., Ag. (3) 20 min., Al (4) 20 min., Ag [Sussi and Raju 1994]. (with permission of Chapman and Hall)

where A and T_0 are constants. A is related to either activation energy or the thermal expansion co-efficient of the free volume²¹. When $T = T_0$ the relaxation time τ becomes infinite and this is interpreted as the glass transition temperature. In the vicinity of and below the glass transition temperature, τ deviates strongly from the VTF law²². In some cases a plot of $\log \tau$ versus $1/T$, when extrapolated, converges to a single point (T_c, τ_c) as shown in Fig.10.12²³. This behavior is expressed by a compensation law according to

$$\tau(T) = \tau_c \exp \frac{\varepsilon}{k} \left(\frac{1}{T} - \frac{1}{T_c} \right) \quad (10.49)$$

where T_c is called the compensation temperature at which all relaxation times have the same value²⁴. Compensation is the relationship between the activation energy and the pre-exponential factor in equation (3.59) expressed as

$$\tau_c = \tau_0 \exp \left(\frac{\varepsilon}{kT_c} \right) \quad (10.50)$$

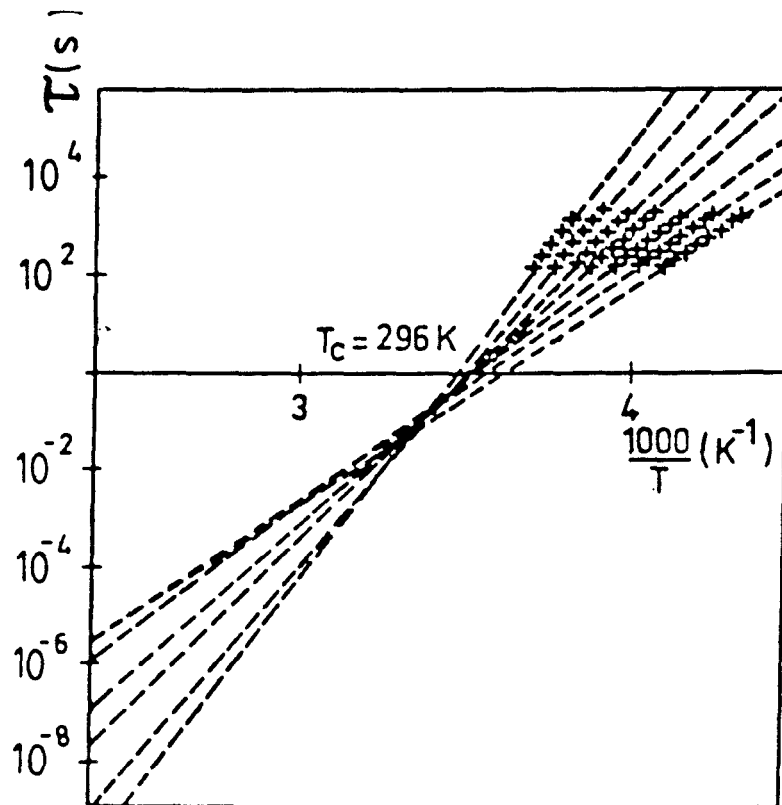


Fig. 10.12 Compensation effect in isotactic polypropylene (Ronarch et. al. 1985, with permission of Am. Inst. Phys.)

According to equation (10.50) a plot of $\ln\tau_0$ versus ε/k gives the reciprocal of the compensation temperature ($-1/T_c$) and the intercept is related to the compensation time τ_c (Fig. 10.13, Colmenero et. al., 1985). The compensation temperature T_c should correspond to the phase transition temperature with good approximation. However a significant departure is observed in semi-crystalline and amorphous polymers as shown in Tables 10.1 and 10.2 (Teysseder, 1997); T_c is observed to be always higher than T_g though the difference is not found to depend systematically on crystallinity. The physical meaning of T_c is not clear though attempts have been made to relate it to changes in the material as it passes from solid to liquid state. Fig. 10.14 shows a collection of the compensation behavior in several polymers; PET data are taken from Teysseder (1997), PPS data are taken from Shimuzu and Nagayama (1993)²⁵. Special mention must be made of Polycarbonate which shows Arrhenius behavior over a wide range of temperatures (b) though at temperatures close to T_g a non-Arrhenius behavior is observed.

10.9 METHODS AND ANALYSES

The methods employed to analyze the TSD currents have been improved considerably though the severe restrictions that apply to the method have not been entirely overcome. The TSD currents obtained in an ideal dielectric with a single peak symmetrical about the line passing through the peak and parallel to the ordinate (y-axis) is the simplest situation. The various relationships that apply here are discussed below.

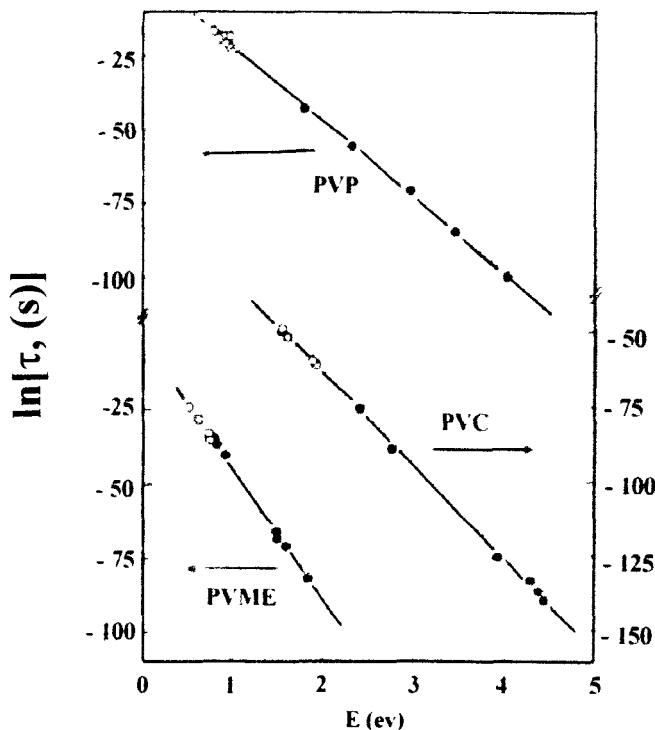


Fig. 10.13 Compensation plots corresponding to poly (N-vinyl-2-pyrrolidone) (PVP), poly(vinylchloride) (PVC), and poly(vinylmethylether) (Colmenero, 1987; with permission of Am. Inst. Phys.)

Table 10.1
Parameters for Various Semicrystalline Polymers (Teyssedre, 1997).
(with permission of Am. Ch. Soc.)

Polymer	X _c %	T _g °C	T _c -T _g (°C)	τ _c (s)
Polypropylene ¹	50	-10	33	2.0×10 ⁻²
VDF ²	50	-42	27	5.8×10 ⁻³
P(VDF-TrFE) 75/25	55	-36	25	3.0×10 ⁻³
65/35 ³	52	-33	22	1.6×10 ⁻²
50/50	48	-28	30	5.0×10 ⁻⁴
Polyamides 12	40	40	44	7.8×10 ⁻³
6.6 ⁴	40	57	48	2.5×10 ⁻²
PEEK	12	144	17	2.0
	31 ⁵	157	8	2.0
PPS ⁶	10	94	24	2.5
PCITrFE ⁷	10	52	74	0.25
PET ⁸	45	100	15	10

X_c% is percentage crystallinity

¹Reference [Ronarch, 1985]

²G. Teyssedre, A. Bernès, C. Lacabanne, J. Poly. Sci: Phys. ed. **31** (1993) 2027

³G. Teyssedre, A. Bernès, C. Lacabanne, J. Poly. Sci: Phys. ed. **33** (1993) 2419

⁴F. Sharif, Ph. D. Thesis, University of Toulouse, 1984

⁵M. Mourgues, A. Bernès, C. Lacabanne, Thermochim. acta, **226** (1993) 7

⁶H. Shimizu, K. Nakayama, J. Appl. Phys., **74** (1993) 1597

⁷H. Shimizu, K. Nakayama, J. Appl. Phys., **28** (1989) L1616

⁸A. Bernès, D. Chatain, C. Lacabanne, Thermochim. Acta, **204** (1992) 69

At low temperatures the term within square brackets in equation (10.21) is small and we can approximate the equation to

$$J = \frac{J_o}{\tau_o} \exp\left(-\frac{\varepsilon}{kT}\right) \quad (10.51)$$

where

$$J_o = \frac{N\mu^2 E_p}{3kT} \quad (10.52)$$

Equation (10.51) has the form of the well known Arrhenius equation and the slope of the log J against 1/T gives the energy. This method is known as the initial rise method²⁶.

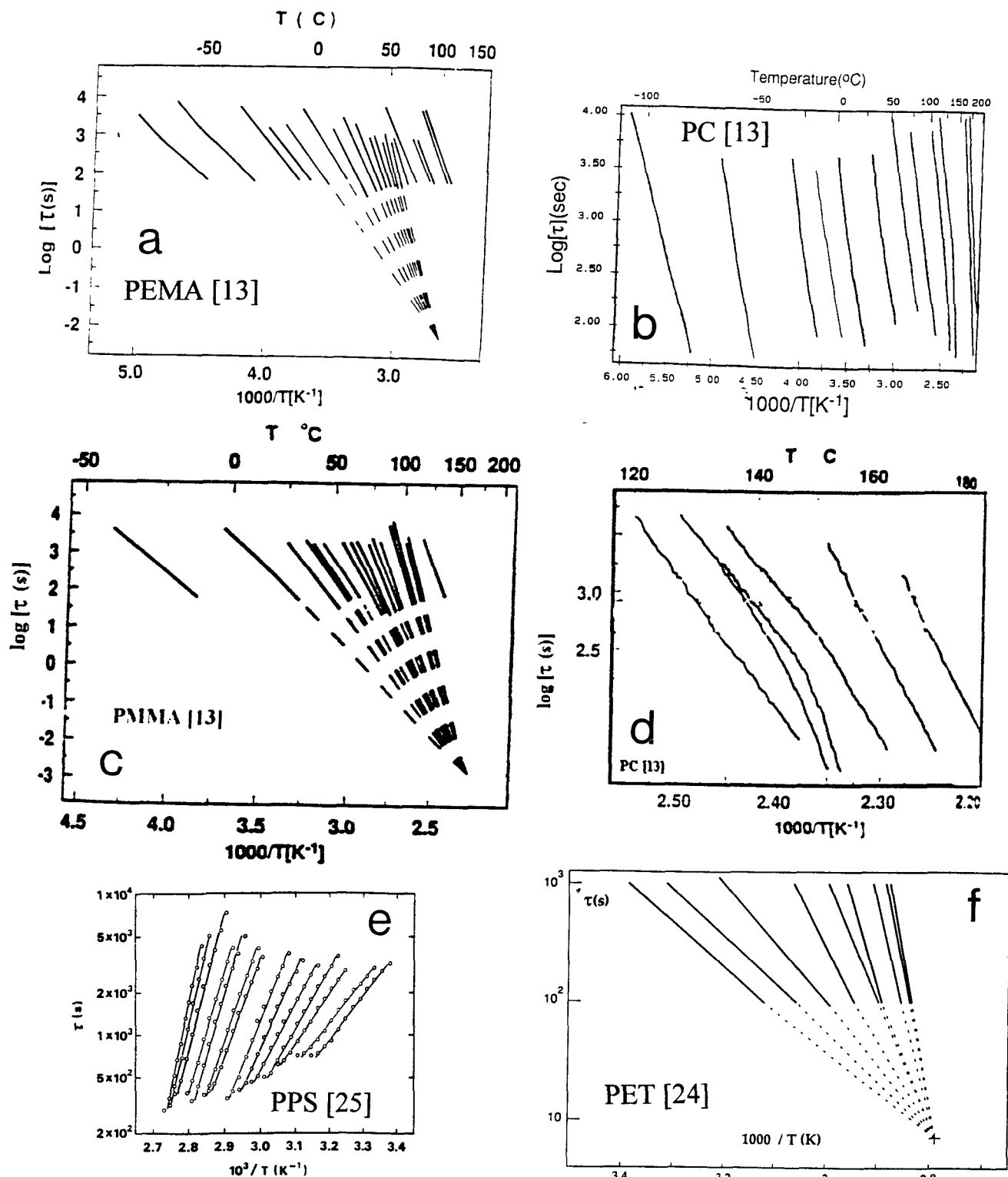


Fig. 10.14 Compensation behavior in several polymers. Polymer and the reference shown on each. (with permission of Polymer: a, b, c, d; Am. Phys. Inst; e; Am. Ch. Inst; f)

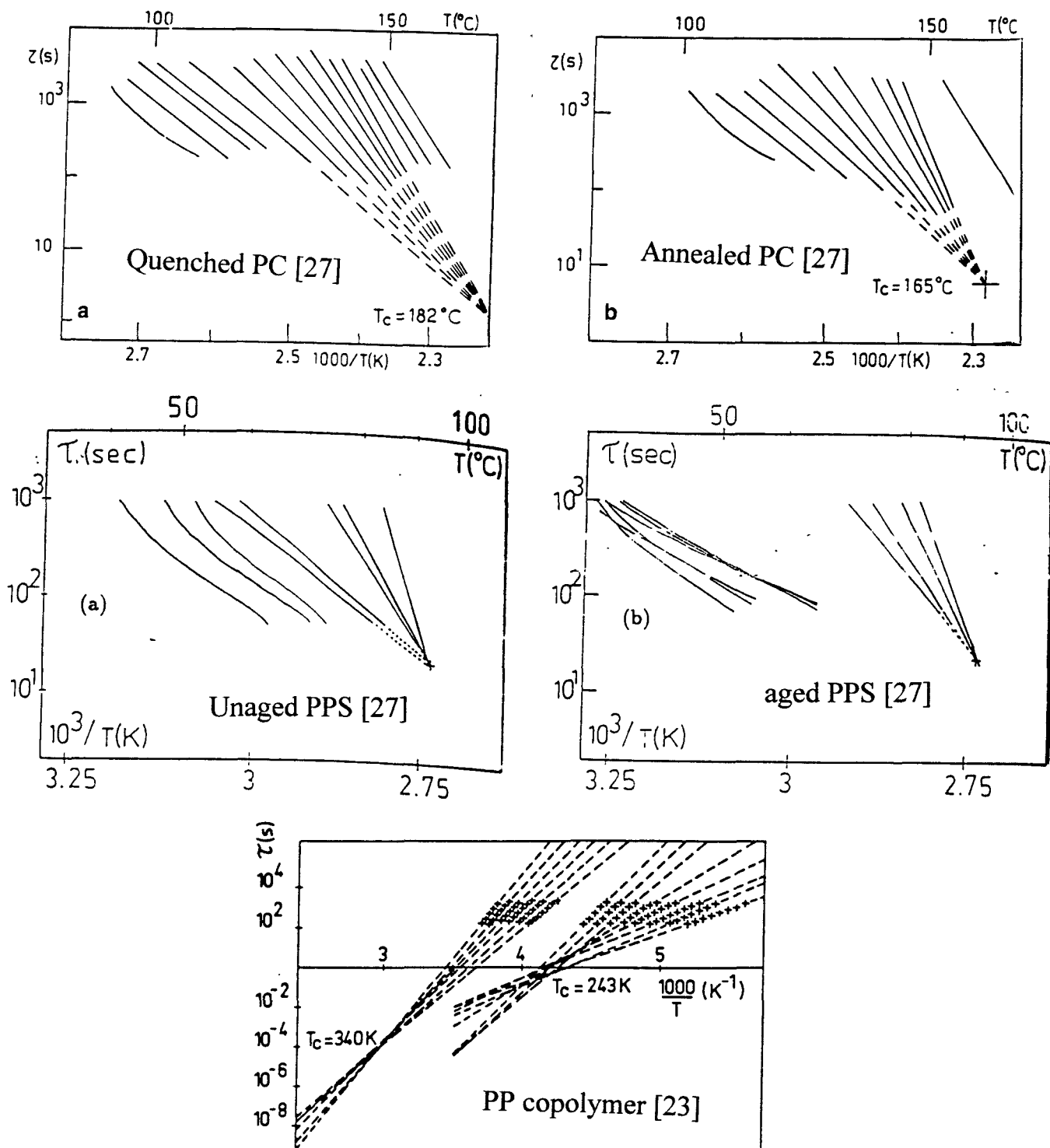


Fig. 10.14 (contd.) Compensation temperature in selected polymers. (g) and (h) in quenched and annealed polycarbonate respectively (Bernès, et al., 1992, with permission of polymer); (j) and (k) in unaged and aged amorphous oriented PPS respectively (Mourgues-Martin, et al., 1992, with permission of IEEE©); (l) Polypropylene block copolymer (Ronarc'h, et al., 1985, with permission of Amer. Inst. Phys.)

Table 10.2

Parameters for various amorphous polymers (Teyssedre, 1997).
(with permission of Am. Ch. Soc.)

Polymer	T_g (°C)	$T_c - T_g$ (°C)	τ_c (s)
Poly(methyl methacrylate) ¹	110	18	0.26
Polystyrene ²	100	2	10
PET ^{3, a}	82	5	6.2
Polycarbonate ⁴	150	32	0.7
PPS ^{5, b}	91	2	36
Polyurethane ⁶	-69	12	0.94
DGEBA-DDS ^{6, c}	133	18	3.2
PEMA ⁷	54	54	6.8×10^{-3}
Poly(vinyl chloride) ⁸	74	10	22
Polyacrylate ⁹	178	25	16
Poly(Vinyl methyl ether) ^{7, 9}	248	15	0.6
Polysulfone ⁹	189	7	4.7

a = Poly(ethylene terephthalate)

b = Poly(p-phenylene-sulphide)

c = Diglycidyl ether of bisphenol A

¹ J. P. Ibar, *Thermochim. Acta*, **192** (1991) 91

² A. Bernès, R. F. Boyer, C. Lacabanne, J. P. Ibar, "Order in the Amorphous state of the Polymers", Ed: S. E. Keinath, R. L. Miller, J. K. Rieke, Plenum, New York, 1986, p. 305

³ A. Bernès, D. Chatain, C. Lacabanne, *Thermochim. Acta*, **204** (1992) 69

⁴ A. Bernès, D. Chatain, C. Lacabanne, *Polymer*, **33** (1992) 4682

⁵ M. Mourgues-Martin, A. Bernès, C. Lacabanne, O. Nouvel, G. Seytre, *IEEE Trans. Elec. Insul.*, **27** (1992) 795

⁶ C. Dessaux, J. Dugas, D. Chatain, C. Lacabanne, *Journées d' Etude de Polymères XXIII*; Toulouse, France, 1995

⁷ B. Sauer, P. Avakian, *Polymer*, **33** (1992) 5128

⁸ J. J. Del Val, A. Alegria, J. Colmenero, C. Lacabanne, *J. Appl. Phys.*, **59** (1986) 3829

⁹ J. Colmenero, A. Alegria, J. M. Alberdi, J. J. Del Val, G. Ucar, *Phys. Rev. B*, **35** (1987) 3995

Evaluation of the parameters in the case of a single peak is relatively simple since the observed peak is due to a single relaxation time. However the analysis is complex when we know that there are several relaxation times and the TSD current due to each process overlaps, resulting in a broad or not well defined peak. The global TSD currents must be separated into its components. To achieve this a peak cleaning method is employed in which the temperature is suddenly lowered to the initial temperature, T_0 , immediately after a peak is observed. A second TSD measurement will then show the subsequent peak which is not a superposition due to the previous peak. Fig. 10.15 shows such a method in which a global curve has been found to be composed of as many as nine separate relaxations²⁷.

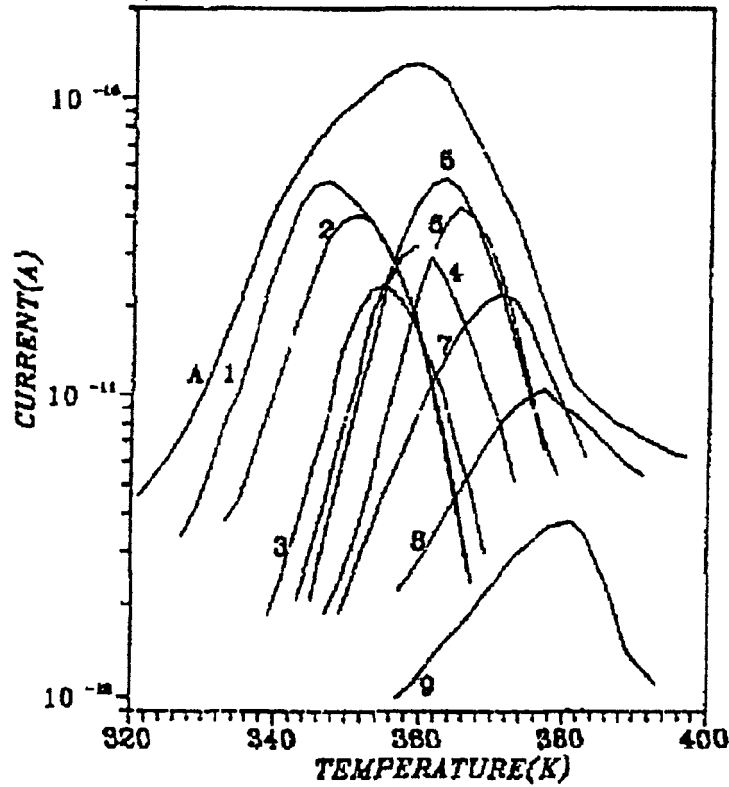


Fig. 10.15 TSD current in amorphous blend of PVC and ABS. Global curve A is composed of several peaks. (Megahed et. al. 1994, with permission of Institute of Physics, England)

A recent technique that has been adopted²⁸ to separate the global TSD curve into its components makes use of a computational procedure. The TSD current expressed by equation (10.21) may be simplified as

$$\ln(I) = b \ln\left(\frac{n}{n_0}\right) + \ln\left(\frac{n_0}{\tau}\right) - \frac{\varepsilon}{kT} \quad (10.53)$$

where b is the order of the kinetics, n the number of carrier in the traps and n_0 the number of initial carriers in the traps. For the first order kinetics, $b = 1$, and for the second order kinetics, $b = 2$. Taking any two arbitrary points on the TSD curve (I_1, T_1) and (I_2, T_2) and substituting these in equation (10.53), then subtracting one resulting equation from the other yields

$$\ln\left(\frac{I_2}{I_1}\right) = b \ln\left(\frac{n}{n_1}\right) - \frac{\varepsilon_a}{k} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (10.54)$$

A similar equation is obtained from a third point (I_3, T_3)

$$\ln\left(\frac{I_3}{I_1}\right) = b \ln\left(\frac{n_3}{n_1}\right) - \frac{\varepsilon_a}{k} \left(\frac{1}{T_3} - \frac{1}{T_1}\right) \quad (10.55)$$

These equations are treated as simultaneous equations with b and ε_a as unknown. The relaxation time is related to the temperature, T_m , at which peak current is observed according to equation (10.22)

$$\tau = \frac{kT_m^2}{\beta \varepsilon_a} \exp\left(-\frac{\varepsilon_a}{kT_m}\right) \quad (10.56)$$

Fan, et al. (1999) adopt the following procedure. Using the high temperature tail of the TSD current-T curve, and equations (10.54), (10.55) and (10.56), the three parameters ε_a , b and τ are determined. Substituting these values in (10.21) an isolated TSD curve is obtained. This curve is subtracted from the global TSD curve and the procedure repeated. The global TSD and separated curves in polyimide are shown in Fig. 10.16.

The relaxation time may be obtained from the TSD curves by employing the relationship

$$\tau(T) = \frac{P(T)}{J(T)} = \int_t^{\infty} \frac{J(t') dt'}{J(t)} \quad (10.57)$$

where $\tau(T)$ is the relaxation time. $J(t)$ is the current density at time t and the numerator is the total charge density remaining in the polarized dielectric²⁹.

Equation (10.57) has been applied in several polymers to determine the relaxation time and compensation parameters. The upper limit of integral in equation (10.57) is infinity, meaning that the TSD currents should be determined till it is reduced to an immeasurably small quantity. However in some of the high temperature materials, as in aramid paper (Raju 1992), it may not be possible to extend the current measurement to such high temperatures. Fig. 10.17 shows the physical meaning of equation (10.57); in a low temperature dielectric which can be heated up to its glass transition temperature, the TSD currents decrease to zero, whereas it is not easy to reach this point in the case of high temperature polymers.

One of the experimental parameters in the measurement of TSD currents is the heating rate, β . By rearranging equation (10.56) the heating rate is expressed as

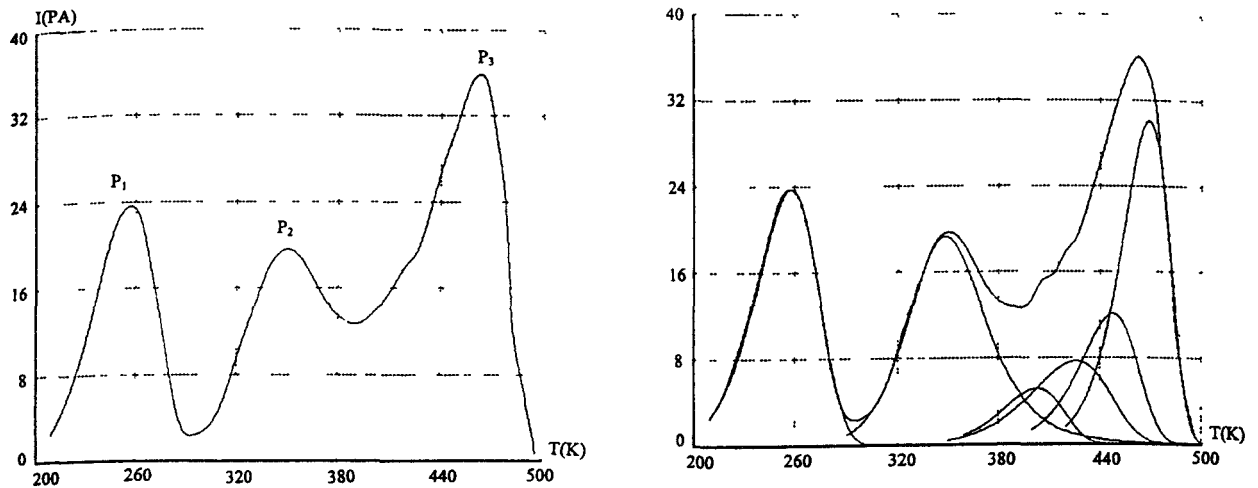


Fig. 10.16 TSD currents in polyimide. (a) global (b) Peak cleaned. (Fan, et al. 1999, with permission of Inst. of Physics, England)

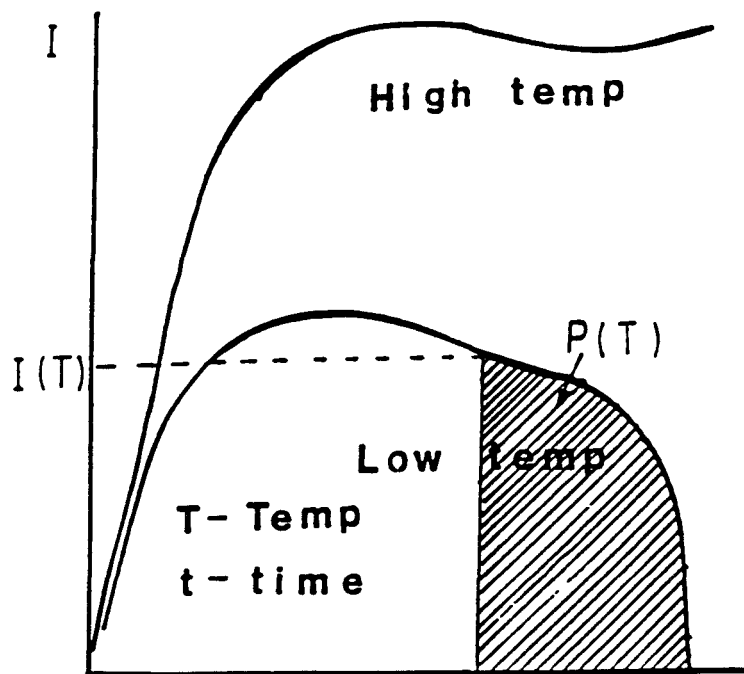


Fig. 10.17 Schematic diagram for calculating the relaxation time from TSD currents. In low temperature polymers the glass transition temperature is reached rendering the TSD current to zero. In high temperature dielectrics there is considerable charge remaining at A.

$$\beta = \left(\frac{k}{\epsilon_a \tau} \right) T_m^2 \exp \left(-\frac{\epsilon_a}{k T_m} \right) \quad (10.56)$$

To determine the remaining charge at the end of the TSD run, as at A in Fig. 10.18 we have to adopt a steady state method to determine the remaining charge. By such a procedure, the released charge and the relaxation time is determined.

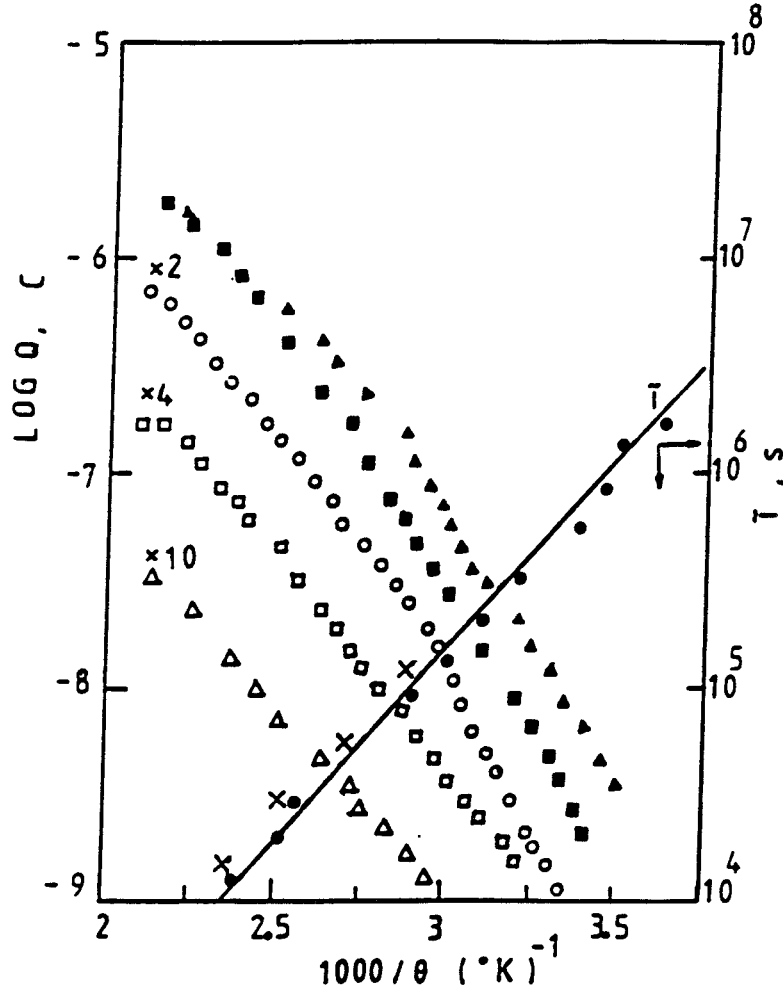


Fig. 10.18 Relaxation time and released charge as a function of $1000/T$ in aramid paper. Poling field and heating rate: $\blacktriangle$ 7.9 MV/m, 1 K/min; $\blacksquare$ 11.8 MV/m, 2 K/min.; $\circ$ 7.9 MV/m, 2 K/min.; $\square$ 3.9 MV/m, 2K/min.; $\triangle$ 2 MV/m, 2K/min.; $\bullet$ 7.9 MV/m, 1 K/min.; $\times$ 1 K/min. (Raju, 1992, with permission of IEEE).

Increasing the heating rate during TSD measurement increases the right side of equation (10.56) by the same amount. This causes T_m to shift upwards. By measuring TSD

currents at two different heating rates β_1 and β_2 and determining T_{m1} and T_{m2} , respectively, the parameters ε_a and τ may be determined. Expressing equation (10.56) twice, one for each heating rate, and taking the ratio we get the activation energy as

$$\varepsilon_a = k \left(\frac{T_{m1} T_{m2}}{T_{m1} - T_{m2}} \right) \ln \left[\frac{\beta_1 \left(\frac{T_{m2}}{T_{m1}} \right)^2}{\beta_2} \right] \quad (10.58)$$

This value of the activation energy may be inserted into equation (10.56) to determine τ . A linear relationship has also been noted, with several linear heating rates as

$$\ln \left(\frac{\tau_m^2}{\beta} \right) = \ln \left(\frac{\varepsilon_a \tau}{k} \right) + \frac{\varepsilon_a}{k T_m} \quad (10.59)$$

A plot of $\ln (\tau_m^2/\beta)$ versus $(1/\tau_m)$ results in a straight line; the slope gives (ε_a/k) and the intercept gives τ .

Careful considerations should be given to identify dipolar relaxation separated from charge carrier traps or from interfacial polarization. To achieve this purpose, TSD currents are measured at various poling fields; a linear variation of the peak current, I_m , with E_p considered to be evidence of dipolar mechanism for polarization. A linear relationship between charge released to the external circuit, this is the integral of $I(T)$ - t curve, with E_p considered to be evidence of dipolar mechanism. In the case of dipolar relaxation measurements, with reversed polarity of E_p , they generate TSD currents that are exact mirror images, since the influence of electrodes in charge injection is negligible.

Fig. 10.19³⁰⁻³⁵ shows a collection of TSD currents in several polymers. TSD spectra are influenced by a number of external factors such as adsorbed gases, moisture, oxidized layers, aged and unaged samples, etc. Notwithstanding the fact that the results are obtained by controlling only a few of these factors, this collection is considered to be appropriate for a quick reference. A comprehensive list of nearly 500 references has been compiled by Lavergne and Lacabanne covering the literature up to the year 1990.

10.10 TSD AND AC DIELECTRIC PROPERTIES

We conclude this chapter by briefly referring to the derivation of the complex dielectric constant $\varepsilon^* = \varepsilon' - j\varepsilon''$ from the TSD spectra. The linking parameter is the relaxation time

τ (T) and the appropriate equations are (3.50) and (3.51) in chapter 3. The dielectric decrement for the i^{th} relaxation process is $\Delta\epsilon_i = (\epsilon_s - \epsilon_\infty)_i$ and it can be evaluated from

$$\Delta\epsilon_i = \frac{1}{\epsilon_0 E} \int_{t_0}^{\infty} J(t) dt = \frac{1}{\epsilon_0 E \beta} \int_{T_0}^T J(T) dT \quad (10.60)$$

The usefulness of equation (10.60) lies in the fact that the dielectric spectra are obtained at sub-harmonic frequencies which is a range at which bridge measurements are not easy to carry out. The data obtained from TSD measurements may be used to examine the low frequency phenomena such as sub- α -relaxation (below T_g) or interfacial polarization. Figs. 10-20 and 10-21 (Shimizu, 1993) show the frequency and temperature dependence of calculated values in PPS. Curves A, B and C of Fig. 10-20 show a sub- T_g relaxation at frequencies of 10^{-9} , 10^{-7} and 10^{-5} Hz respectively at low temperatures as indicated in the legend. At higher temperatures, curves D-G, a sharp peak is observed at T_g due to the α -relaxation. In comparing the derived complex dielectric constant ϵ^* with the measured values, the frequency that is equivalent for comparison is given by equation (10.56), (Van Turnhout, 1975)

$$\tau = \frac{kT_m^2}{\beta\epsilon_a} = \frac{1}{2\pi f_{\text{eq}}} \quad (10.61)$$

From equation (10.61) we obtain the equivalent frequency as

$$f_{\text{eq}} = \frac{\beta\epsilon_a}{2\pi kT_m^2} \quad (10.62)$$

Substituting values appropriate to PPS, $T_m = 370$ K, $\epsilon_a = 2.6$ eV, $\beta = 0.04$ K/s yields $f_{\text{eq}} = 10^{-3}$ Hz. Since the low frequency ac data is usually limited to 1 Hz, the advantages of using the TSD spectra, particularly for sub- T_g relaxation become evident.

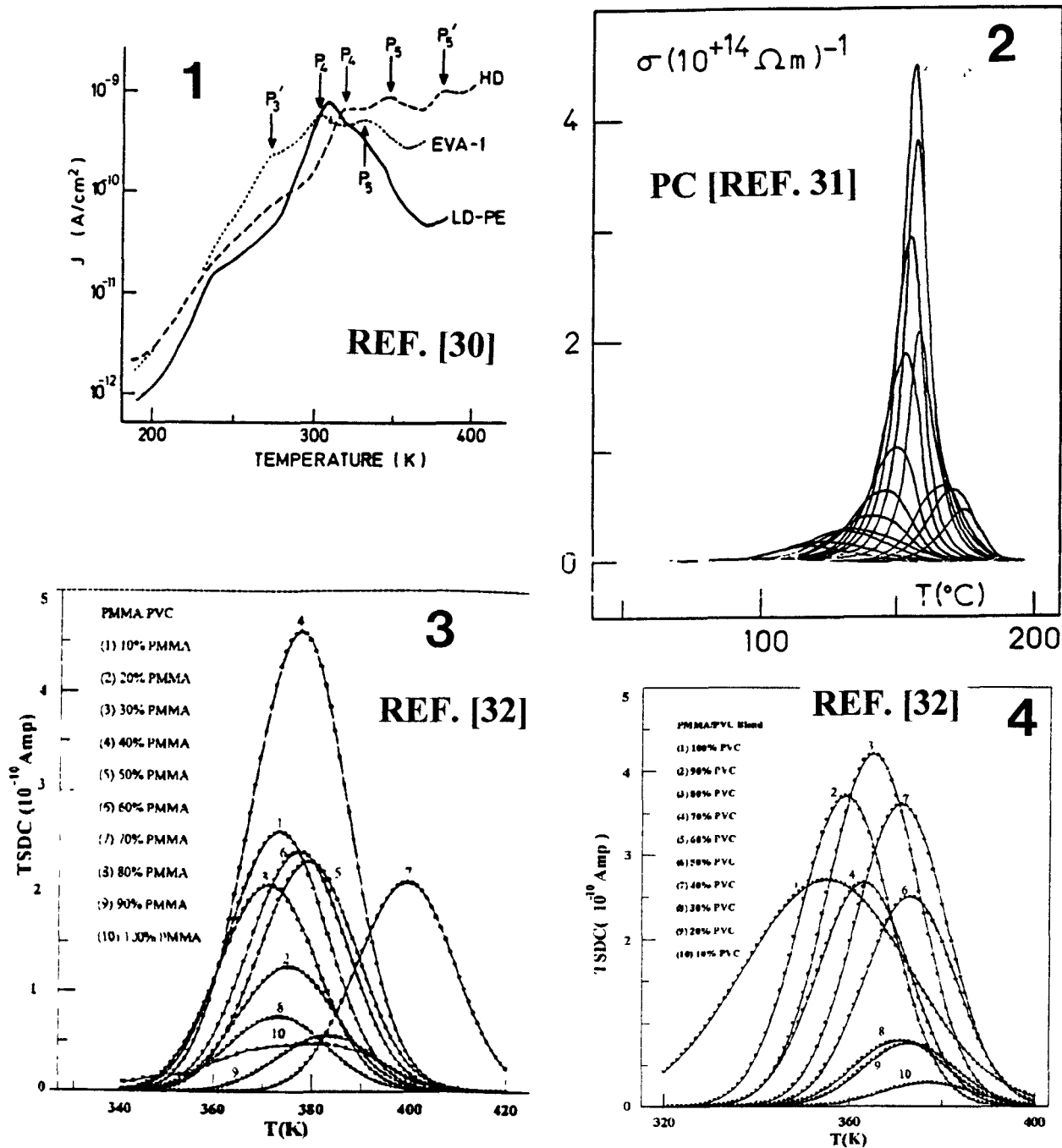
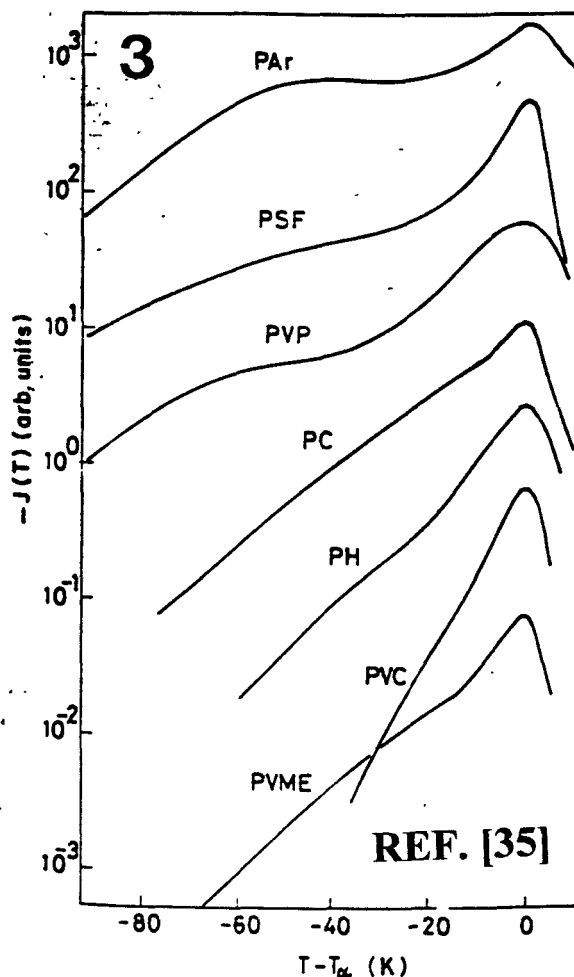
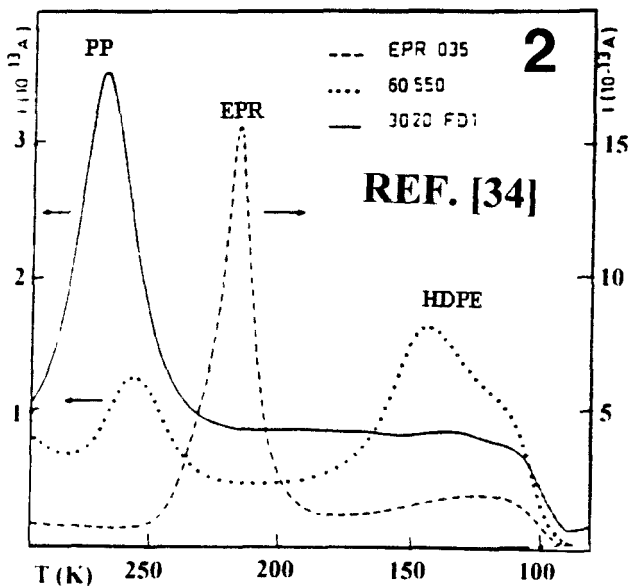
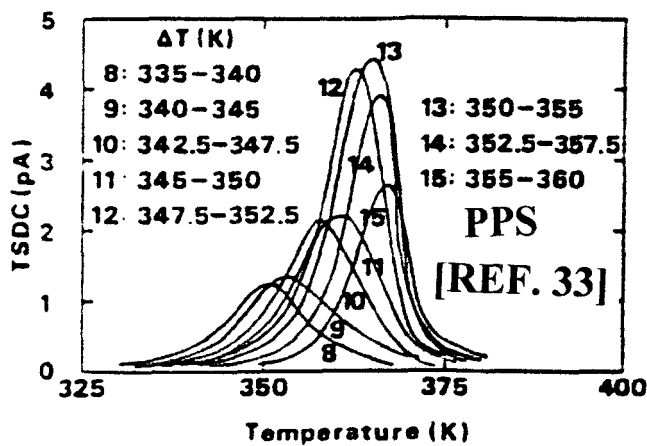
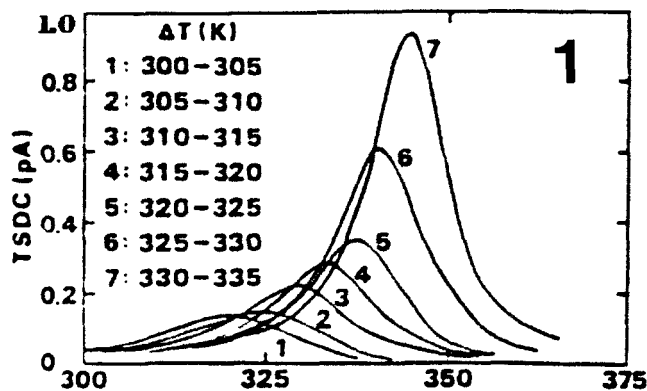


Fig. 10.19 TSD spectra in selected polymers. Sources are indicated by reference number. (with permission: 1-J. Appl. Phys., 2-Polymer, 3 & 4-J. Phys. D: Appl. Phys., England)



PAr-Polyarylate
 PSF-Polysulfone
 PVP-Poly(N-vinyl-2-pyrrolidine)
 PC-Polycarbonate
 PH-Phenoxy
 PVC-Polyvinylchloride
 PVME-Polyvinylmethylether

Fig. 10.19 (contd.) TSD spectra in selected polymers. (With permission: 1 & 2-J. Appl. Phys., 3-Phys. Rev.)

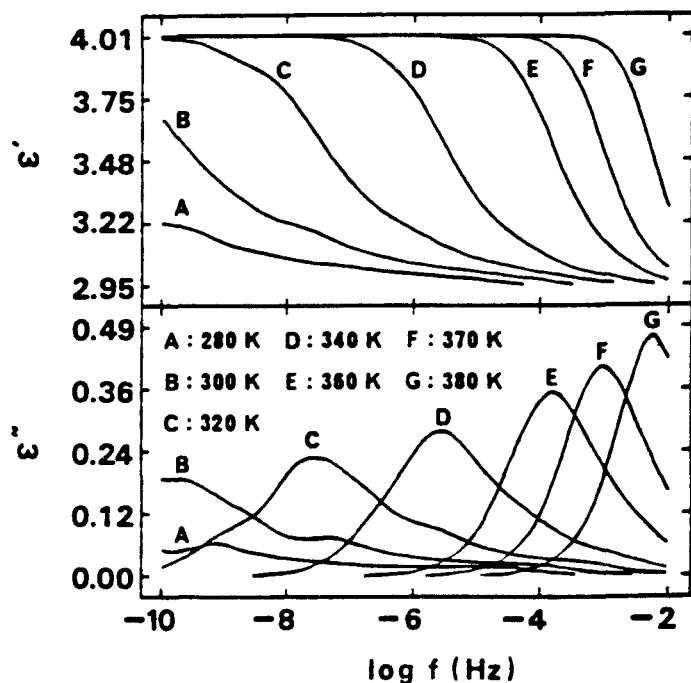


Fig. 10.20 Complex dielectric constant of PPS versus frequency with temperature as the parameter, derived from TSD spectra of Fig. 10.19 (label 1). (Shimizu and Nagayama, 1993; with permission of J. Appl. Phys.)

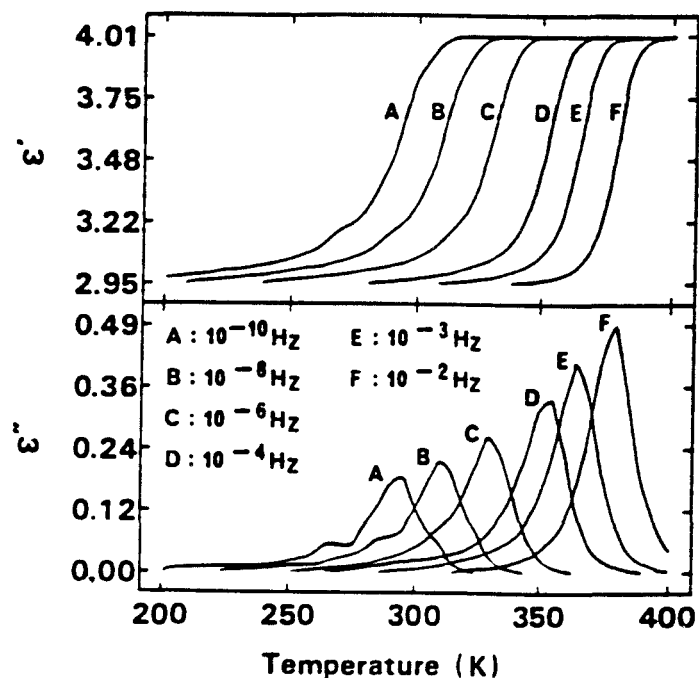


Fig. 10.21 Complex dielectric constant of PPS versus frequency with frequency as the parameter, derived from TSD spectra of Fig. 10.19 (label 1) [33]. (Shimizu and Nagayama, 1993; with permission of J. Appl. Phys.)

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